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POLYCYCLIC AROMATIC HYDROCARBON CONTENT IN WATER AND SEDIMENTS IN THE MIDDLE PART OF SHATT AL-ARAB RIVER- SOUTHERN IRAQ

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This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Polycyclic aromatic hydrocarbons are more carcinogenic and can remain in the water environment by the bioaccumulating in aquatic creatures like fish. The Shatt Al-Arab River begins north of Basrah City at the junction of the Tigris and Euphrates rivers and travels for about 190 kilometers till it reaches the Arabian Gulf. The current study included measuring the concentrations of polycyclic aromatic hydrocarbons (PAHs) in water and sediments of three sites chosen from the middle part of the Shatt Al-Arab River (Al-Ashar, Al-Karmah, and Al-Deir), and some environmental factors were measured, which included (Water Temperature, Dissolved Oxygen, pH, Electrical Conductivity, Salinity and Turbidity). The results of the current study showed that the concentrations of polycyclic aromatic hydrocarbons in water ranged between 6.01-21.7 ng/L, as well as the concentrations in sediments were ranged between 14.6 – 52.5 ng/g D.W. On the other hand the highest concentrations of PAHs appeared during winter while the lowest concentrations appeared during summer. Furthermore, the concentrations of polycyclic aromatic hydrocarbons in water and sediments were affected by the sites, seasons and a number of studied environmental factors, where the temperature was the most important factor.

Keywords: Shatt Al-Arab River; polycyclic aromatic hydrocarbons; water; sediments.

1. INTRODUCTION

Hydrocarbons enter the aquatic environment either anthropogenic resources which occurred by discharge of petroleum products such as spillages, tanker operations, industrial effluents, refineries, transport of petroleum products, uncontrolled releases from power plants, accidental discharges, municipal waste discharges, or biogenic resources which occurred by

decomposition of organisms containing biogenic hydrocarbons or by natural seepage [1,2].

Although many aquatic organisms of Shatt Al-Arab River that including fish, plants, zooplankton, algae and bacteria are capable to synthesize biogenic hydrocarbons, a large proportion is derived from human activities [3]. (According to the reviewer, it is already present in reference No. 3).

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One of the most dangerous pollutant for aquatic environment is petroleum hydrocarbons and its derivatives because they are potentially carcinogenic materials especially PAHs compounds [4].

Polycyclic aromatic hydrocarbons are classified into two groups, the first group is included high molecular weight PAHs (HMW), that are consist four or more rings and are less readily bio degraded by microorganisms, hence can persist in the aqueous environment by bio-accumulating in aquatic organisms like fish and are more carcinogenic [5]. The second group is included low molecular weight (LMW) PAHs that consists two or three aromatic rings, although less carcinogenic also have toxic effect on aquatic organisms [6]. Long term exposure to hydrocarbon compounds can cause various disturbances of human health, where human exposure to PAHs can causes cancer, mutations and birth defects [7,8,9]. In aquatic environments, they float and prevent the oxygen exchange and reduce the penetration of sunshine to the deep phytoplankton, consequently reduce of photosynthesis [10].

Shatt Al-Arab River consists of the confluence of the Tigris and Euphrates rivers north of Basrah City and runs for about 190 km until it flows into the Arabian Gulf [11]. The waters of Shatt Al-Arab River are affected by the two half-day tidal waves coming from the Arabian Gulf during more than 24 hours [12]. The drainage of Shatt Al-Arab River waters range between (246-2923 m³/s) [13].

Al-Hejuje at 2014 took on her study the concentrations of total petroleum hydrocarbons and polycyclic aromatic compounds in the water of five sites in the middle part of Shatt Al-Arab River, the

concentrations of (PAHs) compounds in the water were ranged between 5.81- 47.96 ng/l and in sediment ranged between 4.3-28.48 ng/g D.W. [14]. Moreover, Al-Hejuje at 2019 study showed a clear effect of environmental factors on the concentrations of polycyclic aromatic compounds, which ranged between 3.62-31.25 ng/l of water and ranged between 6-70 ng/l D.W for sediment [15].

The present study aimed to determine the concentrations of aromatic hydrocarbons contents in water and sediment as well as evaluate the water quality of Shatt Al-Arab River.

2. MATERIALS AND METHODS

Water and sediments samples were collected from three sites (Al-Ashar, Al-Karma, and Al-Dair) in winter and summer (2019). Where the sediment samples were collected by using a grab sampler the sample was placed in dark bags, then the samples were placed in a cooler box for transportation to the laboratory, After which the samples were dried, crushed, and sieved with a sieve (63 microns) to be prepared for measurement. On the other hand, about 20 g of sediment was taken for each measurement.

Surface water samples were collected (20-30 cm) deep below the surface of the water in the middle of the river during the period of the low tide. About (5 liters) of water were collected from each site by the dark glass as well as about (1.5 liters) were collected and transferred to the laboratory for turbidity Measuring. While, water temperature, pH, and salinity were conducted in the field using a WTW multi-meter. All the samples were transferred directly to the laboratory in a cool box.



Fig. 1. Study sites

Hydrocarbons were extracted according to [16] (16 Analysis method) of water and according to [17] (17 Analysis method) of sediment, then Polycyclic Aromatic Hydrocarbons were measured with Gas Chromatography.

Data were statistically analyzed using the analysis of variance (ANOVA). Data were collected statistically using the software SPSS, below the probability level of 0.05.

3. RESULTS AND DISCUSSION

3.1 Physical and Chemical Parameters

Water temperature in the current study ranged between 14 – 34 C° and there were significant differences at $P < 0.05$ between seasons and sites (Table 1). Water temperature is one of the most important indicators of water quality because it effects of the physical, chemical and biological characteristics of the aquatic environment, where the temperature effect on the distribution of organisms in environment [18]. Naturally, it increased during the summer and decreased during the winter, in the present study there were significant differences at $P < 0.05$ between the seasons, and this due to the nature of the climate of Iraq in general, it's hot and dry in the summer and cool rainy in the winter, which is characterized by thermal extremism and the length of the hot season [14,19,20].

pH values ranged between 7.37-8.01 . Normally, pH increase in the winter due to surface removal of the alkaline materials by rain, while a decrease during summer because increasing of decomposition of organic materials by microorganisms and the production of dissolved carbon dioxide [21,22,23,24] , On the other hand , in the present study there were not significant differences between seasons , this may be due to surface removal of alkaline materials with flow of water from Iran by Al-Swaib River until the beginning of summer2019. On the other hand, the results of pH were within the allowable limits 6.5-8.5 [25].

In the present study electrical conductivity values ranged between 2.97-4.01 msm/cm, While salinity between 1.4-2.3 PSU Table 1. In the current study there were significant differences $P < 0.05$ between seasons and sites for both electrical conductivity and salinity. The high electrical conductivity and salinity levels during winter may be due to the low flow of water during autumn / 2019 and the movement of the salt water from Arabian gulf towards Shatt Al-arab River, which continued to affect winter with a decrease in the rate of rainfall, while the rate of rain

increased significantly in spring / 2019 and the entry of huge water bodies from the Tigris and Euphrates Rivers and from the Iranian side across the Al-Swaib River and push the salt water towards to the Arabian Gulf and led to a decrease in the percentage of salts and the water continued to flow from the Al-Swaib River until the beginning of summer.

Rasolofomanana at 2009 emphasized the salinity correlation closely with electrical conductivity, since salinity expresses the content of dissolved salts, and this is confirmed by the current study as it found a significant correlation between them ($r=0.965$) [26].

Turbidity values ranged between 4.49-72 NTU and there were significant differences $P < 0.05$ between seasons and sites (Table 1). Turbidity in water is caused by suspending particles or colloidal substances that impede the transmission of light through water, and may be caused by organic or inorganic materials or a mixture of the two, as well as what the World Health Organization (2011) indicated that there is a link to microorganisms (bacteria and viruses) are usually particles. The decrease in value in winter is due to the weak water flow in autumn, which extended into the winter during that period, While, The reason for the high turbidity in summer may be due to increased drainage of water from Tigris, Euphrates and Al-swaib River, which continued until summer/2019, which has caused movement various types of particles in the water column [27].

3.2 Polycyclic Aromatic Hydrocarbons (PAHs)

The highest concentration of PAHs compounds in water 21.7 ng/L during winter and the lowest concentration 6.01 ng/L during summer (Table 2). Statistical analysis showed the presence of significant differences between seasons $P < 0.05$ and no significant differences between sites $P > 0.05$.

There was an inverse correlation relationship ($r = -0.865$) between concentrations of PAHs in water and recorded temperatures, as they decreased during summer and increased during winter, due to the evaporation of some PAHs from water during summer as a result of high temperatures [15,29] , and high temperatures also stimulate microorganisms to break down these compounds by the biodegradation process, especially low molecular weights [30,31]. Also, photo-oxidation increases further due to intense solar radiation. Increased PAH concentrations during the winter season owing to lesser PAH evaporation and decreased microorganism activity for analyzing these chemicals at cold temperatures [32]. Also, because of the increased use of fuel for heating, as

Table 1. Physical and chemical parameters in present study

Seasons	Stations	Parameters					
		Temp. (C°)	pH	EC (mSm/cm)	Sali. (PSU)	DO (mg/l)	Tur. (NTU)
Winter	Al-Ashar	15	7.44	4.01	2.3	8	20.3
	Al-karma	14.5	8.01	3.83	2.1	6.6	6.93
	Al-Daier	14	7.37	3.11	1.6	7	4.49
Summer	Al-Ashar	32	7.96	3.22	1.5	5	21
	Al-arma	34	7.61	2.97	1.4	6	56.6
	Al-Daier	30	7.58	3.29	1.5	6	72
The Total World Permissible values		-	6.5-8.5 [27]	0.25 mS/cm [28]	-	5 mg/L [27]	5 NTU [27,28]

well as the involvement of rain and highway runoff, aromatic compounds penetrate the environment considerably during the winter [33,34].

It was observed from the results that there is an inverse relationship between the concentrations of PAHs in water and turbidity ($r = -0.743$), due to the association of PAHs with suspended particles in the water column and precipitation leads to a decrease in the concentrations of PAHs in water, and this was consistent with both [14,15].

The results of the current study showed that the compounds of PAHs prevalent in water are Benzo (b) fluoranthene, Benzo (k) fluoranthene, Benz (a) pyrene, and lower ratio of Pyrene and Indeno (1,2,3-cd) pyrene + Dibenz (a, h) anthracene, Chrysene, Benz (a) pyrene, Benzo (g, h, i) perylene.

The highest concentration of PAHs compounds in sediments was 52.5 ng/L during winter and the lowest concentration was 14.6 ng/L during summer (Table 2). Statistical analysis showed that there were significant differences between season and between sites $P > 0.05$.

The results of the study, shown in Table (2), showed high concentrations during winter was 52.5 ng/g Dry Weight (D.W) and low during summer was 14.6 ng/g D.W, this due to their correlation with PAHs

concentrations in water, which are positively correlated with water temperature during winter and summer. The results of the current study showed that the concentrations of PAHs in sediments were higher than those in water, as a result of photo oxidation and sedimentation of PAHs from the water column to the bottom as well as the degradation of PAHs of low molecular weight in the water column [35,36].

Al-Ashar site had the highest concentration of PAHs in sediments during winter and summer compared to the other two sites, and this may be due to the proximity of the site to the city center and proximity to the main road adjacent to Shatt Al-Arab River. Where affected by atmospheric deposition of PAHs, sanitary sewer and roadway runoff and this consistent with [37], in addition to the site is active in the movement of boats and small ships, which add PAHs to water in this side.

Because hydrocarbons in the aquatic environment tend to adsorb to the surfaces of particles and suspended materials in the water column, concentrations of PAHs in sediments were greater than in water, causing them to sink to the bottom [14]. Sediments are still contaminated with petroleum hydrocarbons and other organic contaminants, posing a serious health danger to many of the ecosystem's aquatic creatures [38].

Table 2. Total concentrations of PAHs (ng/L) in water and sediment (ng/g D.W) for the study sites during the study period

Seasons	Site	PAHs in water	PAHs in sediment
Winter	Al-Ashar	21.7	25.9
	Al-karma	14.7	14.6
	Al-Daier	15.2	21.8
Summer	Al-Ashar	9.97	52.5
	Al-karma	6.41	18.7
	Al-Daier	6.01	49.9
The Total World Permissible values		1 ng/L - 11 µg/L [27]	-
The Total World Permissible values		-	16770 ng/g [28]

The results of the current study showed that the PAHs predominant in sediments are Benzo (b) fluoranthene, Benzo (k) fluoranthene and Benz (a) pyrene, while the lower ratio were Pyrene and Indeno (1,2,3-cd) pyrene + Dibenz (a, h) anthracene, Chrysene, Benz (a) pyrene, Fluoranthene, Benzo (g, h, i) perylene, Phenanthrene and Benzo (a) anthracene. In the current study, the reason for the dominance of (Benzo (b) fluoranthene, Benzo (k) fluoranthene and Benz (a) pyrene) because they are of high molecular weight, which makes them resistant to [39].

4. CONCLUSION

Sites, seasons, and the number of analyzed environmental parameters all influenced the concentrations of polycyclic aromatic hydrocarbons in water and sediments, with the temperature being the most relevant component. Where the Al-Ashar site sediments and water showed the highest concentration of PAHs in the summer and winter seasons.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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